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(54) Title: IMPROVED CONVERSION OF SYNGAS FROM FISCHER-TROPSCH PRODUCTS VIA OLEFIN METATHESIS

(57) Abstract: A process for preparing distillate fuel compositions from a C₂₋₆ olefinic fraction and a C₂₀₊ fraction via molecular averaging is described. The fractions can be obtained, for example, from Fischer-Tropsch reactions, and/or obtained from the distillation or other processing of crude oil. Molecular averaging converts the fractions to a product that includes a significant fraction in the C₅₋₂₀ range that can be used for preparing a distillate fuel composition. The product is preferably isomerized to increase the octane value and lower the pour, cloud and smoke point. The product can also be hydrotreated and/or blended with suitable additives for use as a distillate fuel composition.

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1 IMPROVED CONVERSION OF SYNGAS
2 FROM FISCHER-TROPSCH PRODUCTS
3 VIA OLEFIN METATHESIS

FIELD OF THE INVENTION

7 This invention relates to the olefination and subsequent molecular averaging
8 of the waxy fraction resulting from Fischer-Tropsch synthesis.

BACKGROUND OF THE INVENTION

12 The majority of distillate fuel used in the world today is derived from crude oil.
13 Crude oil is in limited supply, includes aromatic compounds believed to cause
14 cancer, and contains sulfur and nitrogen-containing compounds that can
15 adversely affect the environment. For these reasons, alternative methods for
16 generating distillate fuel have been developed.

18 One alternative method for generating distillate fuel involves converting
19 natural gas, which is mostly methane, to synthesis gas (syngas), which is a
20 mixture of carbon monoxide and hydrogen. The syngas is converted to a
21 range of hydrocarbon products, collectively referred to as syncrude, via
22 Fischer-Tropsch synthesis.

24 It is generally possible to isolate various fractions from a Fischer-Tropsch
25 reaction, for example, by distillation. The fractions include a gasoline fraction
26 (B.P. about 68-450°F/20-232°C), a middle distillate fraction (B.P. about
27 250-750°F/121-399°C), a wax fraction (B.P. about 650-1200°F/343-649°C)
28 primarily containing C₂₀ to C₅₀ normal paraffins with a small amount of
29 branched paraffins and a heavy fraction (B.P. above about 1200°F/649°C)
30 and tail gases.

31

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1 An advantage of using fuels prepared from syngas is that they do not contain
2 significant amounts of nitrogen or sulfur and generally do not contain aromatic
3 compounds. Accordingly, they have minimal health and environmental
4 impact.

5

6 However, a limitation associated with Fischer-Tropsch chemistry is that it tends
7 to produce a broad spectrum of products, ranging from methane to wax.
8 While the product stream includes a fraction useful as distillate fuel, it is not
9 the major product.

10

11 Fischer-Tropsch products tend to have appreciable amounts of olefins in the
12 light fractions (i.e., the naphtha and distillate fuel fractions), but less so in the
13 heavy fractions. Depending on the specifics of the Fischer-Tropsch process,
14 the naphtha can be expected to include more than 50% olefins, most of which
15 are alpha olefins. Distillate fuels will also contain some level of olefins
16 (typically between 10 and 30%) and the distillate waxy fractions can contain
17 smaller quantities.

18

19 One approach for preparing distillate fuels is to perform Fischer-Tropsch
20 synthesis at high alpha values that minimize the yield of light gases, and
21 maximize the yield of heavier products such as waxes. The wax from the
22 Fischer-Tropsch process typically causes the entire syncrude to be a solid
23 even at high temperatures, which is not preferred. The waxes are then
24 hydrotreated and hydrocracked to form distillate fuels. Since hydrocracking is
25 performed at relatively high temperatures and pressures, it is relatively
26 expensive.

27

28 It would be advantageous to provide a process which provides useful distillate
29 fuels from Fischer-Tropsch products but which does not require a
30 hydrocracking step. The present invention provides such a process.

31

1

SUMMARY OF THE INVENTION

2

3 In its broadest aspect, the present invention is directed to an integrated
4 process for producing distillate fuels, including jet fuel, gasoline and diesel.
5 The process involves the partial dehydrogenation of the wax fraction and/or
6 heavy fraction of a Fischer-Tropsch reaction to form olefins, which are reacted
7 with the olefins in the naphtha and/or light gas fraction of the Fischer-Tropsch
8 reaction in the presence of an olefin metathesis catalyst. The resulting
9 product has significantly less wax, and the product has an average molecular
10 weight between the molecular weight of the naphtha and/or light gas fractions
11 and the molecular weight of the wax and/or heavy fractions.

12

13 Fractions in the distillate fuel range can be isolated from the reaction mixture,
14 for example, via fractional distillation. The product of the molecular averaging
15 reaction tends to be highly linear, and is preferably subjected to catalytic
16 isomerization to improve the octane values and lower the pour, cloud and
17 freeze points. The resulting composition has relatively low sulfur values, and
18 relatively high octane values, and can be used in fuel compositions.

19

20 In one embodiment, one or both of the feeds to the molecular averaging
21 reaction is isomerized before the molecular averaging reaction. Incorporation
22 of isoparaffins into the molecular averaging reaction provides a product
23 stream that includes isoparaffins in the distillate fuel range which have
24 relatively high octane values.

25

26 In another embodiment, the alpha olefins in the light naphtha and gas are
27 converted into internal olefins (either normal internal or iso-internal olefins).
28 When these materials are averaged against the internal olefins derived from
29 dehydrogenation of the wax, the yield of intermediate fuels is increased.
30 Furthermore, the light naphtha and gas fractions may contain impurities such
31 as alcohols and acids. These oxygenates can be converted to additional

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- 1 olefins by dehydration and decarboxylation. Traces of other impurities should
- 2 be reduced to acceptable levels by use of adsorbents and/or extractants.

3

4 Preferably, after performing Fischer-Tropsch synthesis on syngas, and before
5 performing the molecular averaging reaction, hydrocarbons in the distillate
6 fuel range are separately isolated, for example, via fractional distillation. The
7 wax and/or heavy fraction are then dehydrogenated, the naphtha and/or light
8 gas fractions are added to the resulting olefinic mixture, and reaction mixture
9 is molecularly averaged by subjecting the olefins to olefin metathesis

1

12 It is preferred that the wax and/or heavy fraction and the naphtha and/or light
13 gas fractions are derived from Fischer-Tropsch synthesis. However, at least a
14 portion of the low molecular weight olefins or the waxy fraction can be derived
15 from a source other than Fischer-Tropsch synthesis. Due to the nature of the
16 molecular averaging chemistry, the reactants cannot include appreciable
17 amounts (i.e., amounts that would adversely affect the catalyst used for
18 molecular averaging) of thiols, amines, or cycloparaffins.

10

20 It may be advantageous to take representative samples of each fraction and
21 subject them to molecular averaging reactions, adjusting the relative
22 proportions of the fractions until a product with desired properties is obtained.
23 Then, the reaction can be scaled up using the relative ratios of each of the
24 fractions that resulted in the desired product. Using this method, one can "dial
25 in" a molecular weight distribution which can be roughly standardized between
26 batches and result in a reasonably consistent product.

21

BRIEF DESCRIPTION OF THE DRAWINGS

3

30 The Figure is a schematic flow diagram representing one embodiment of the
31 invention.

32

1 DETAILED DESCRIPTION OF THE INVENTION
2

3 In its broadest aspect, the present invention is directed to an integrated
4 process for producing distillate fuels, such as jet fuel, gasoline and diesel fuel.
5 The process involves the partial dehydrogenation of the wax fraction and/or
6 heavy fraction of a Fischer-Tropsch reaction mixture to form olefins, which are
7 reacted with the olefins in the naphtha and light gas fraction of the
8 Fischer-Tropsch reaction in the presence of an olefin metathesis catalyst.
9 The resulting product has significantly less wax, and has an average
10 molecular weight between the molecular weight of the naphtha and/or light
11 gas fractions and the molecular weight of the wax and/or heavy fractions.

12 Hydrocarbons in the distillate fuel range can be isolated from the reaction
13 mixture via fractional distillation. The product of the molecular averaging
14 reaction tends to be highly linear, and is preferably subjected to catalytic
15 isomerization to improve the octane values and lower the pour, cloud and
16 freeze points. To maximize the yield of desired distillate fuels, the olefins in
17 the light naphtha can first be converted to internal olefins.

18
19 In one embodiment, at least a portion of one or both of the relatively low
20 molecular weight (for example, C₂₋₆) and/or relatively high molecular weight
21 (for example, C₂₀₊) fractions is obtained from another source, for example, via
22 distillation of crude oil.

23
24 The process described herein is an integrated process. As used herein, the
25 term "integrated process" refers to a process which involves a sequence of
26 steps, some of which may be parallel to other steps in the process, but which
27 are interrelated or somehow dependent upon either earlier or later steps in the
28 total process.

29
30 An advantage of the present process is the effectiveness and relatively
31 inexpensive processing costs with which the present process may be used to

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1 prepare high quality distillate fuels, and particularly with feedstocks which are
2 not conventionally recognized as suitable sources for such fuels. An
3 additional advantage is that the resulting fuel is highly paraffinic, and has
4 relatively low levels of sulfur, nitrogen and polynuclear aromatic impurities.

5

6 Distillate Fuel Composition

7

8 The distillate fuel prepared according to the process described herein typically
9 has an average molecular weight in the C₅₋₂₀ range. The molecular weight
10 can be controlled by adjusting the molecular weight and proportions of the
11 high molecular weight (wax and/or heavy fraction) and the low molecular
12 weight (naphtha and/or light gas) fractions. Distillate fuel compositions with
13 boiling points in the range of between about 68-450°F, more preferably
14 between about 250-370°F, are preferred. The currently most preferred
15 average molecular weight is around C₈₋₁₂, which has a boiling point in the
16 range of roughly 345°F, depending on the degree of branching.

17 Specifications for the most commonly used diesel fuel (No. 2) are disclosed in
18 ASTM D 975 (See, for example, p. 34 of 1998 Chevron Products Company
19 Diesel Fuels Tech Review). The minimum flash point for diesel fuel is 52°C
20 (125°F). Specifications for jet fuel are disclosed in ASTM D 1655, standard
21 Specification for Aviation Turbine Fuels. The minimum flash point for jet fuel
22 is typically 38°C.

23

24 The process is adaptable to generate higher molecular weight fuels, for
25 example, those in the C₁₅₋₂₀ range, or lower molecular weight fuels, for
26 example, those in the C₅₋₈ range. Preferably, the majority of the composition
27 includes compounds within about 8, and more preferably, within about
28 5 carbons of the average.

29

30 Another important property for the distillate fuel is that it has a relatively high
31 flash point for safety reasons. Preferably, the flash point is above 90°C, more

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1 preferably above 110°C, still more preferably greater than 175°C, and most
2 preferably between 175°C and 300°C.

3

4 The distillate fuel can be used, for example, in diesel automobiles and trucks.
5 The high paraffinic nature of the fuel gives it high oxidation and thermal
6 stability. The fuel can also be used as a blending component with other fuels.
7 For example, the fuel can be used as a blending component with fuels derived
8 from crude oil or other sources.

9

10 Preferably, the reactants used in the molecular averaging reaction are
11 obtained from Fischer-Tropsch reactions, and therefore, contain virtually no
12 heteroatoms or aromatic compounds. Alternatively, the fuel can be obtained
13 by molecular averaging of other feedstocks, preferably in which at least the
14 heteroatoms, and more preferably the aromatics, have been removed.

15

16 Additives

17

18 The distillate fuel composition can include various additives, such as
19 lubricants, emulsifiers, wetting agents, densifiers, fluid-loss additives,
20 corrosion inhibitors, oxidation inhibitors, friction modifiers, demulsifiers,
21 anti-wear agents, anti-foaming agents, detergents, rust inhibitors and the like.
22 Other hydrocarbons, such as those described in U.S. Patent No. 5,096,883
23 and/or U.S. Patent No. 5,189,012, may be blended with the fuel, provided that
24 the final blend has the necessary octane/cetane values, pour, cloud and
25 freeze points, kinematic viscosity, flash point, and toxicity properties. The
26 total amount of additives is preferably between 50-100 ppm by weight for
27 4-stroke engine fuel, and for 2-stroke engine fuel, additional lubricant oil may
28 be added.

29

1 Diesel fuel additives are used for a wide variety of purposes; however, they
2 can be grouped into four major categories: engine performance, fuel stability,
3 fuel handling, and contaminant control additives.

4

5 Engine performance additives can be added to improve engine performance.
6 Cetane number improvers (diesel ignition improvers) can be added to reduce
7 combustion noise and smoke. 2-Ethylhexyl nitrate (EHN) is the most widely
8 used cetane number improver. It is sometimes also called octyl nitrate. EHN
9 typically is used in the concentration range of 0.05% mass to 0.4% mass and
10 may yield a 3 to 8 cetane number benefit. Other alkyl nitrates, ether nitrates
11 some nitroso compounds, and di-tertiary butyl peroxide can also be used.

12

13 Fuel and/or crankcase lubricant can form deposits in the nozzle area of
14 injectors — the area exposed to high cylinder temperatures. Injector
15 cleanliness additives can be added to minimize these problems. Ashless
16 polymeric detergent additives can be added to clean up fuel injector deposits
17 and/or keep injectors clean. These additives include a polar group that bonds
18 to deposits and deposit precursors and a non-polar group that dissolves in the
19 fuel. Detergent additives are typically used in the concentration range of
20 50 ppm to 300 ppm. Examples of detergents and metal rust inhibitors include
21 the metal salts of sulfonic acids, alkylphenols, sulfurized alkylphenols, alkyl
22 salicylates, naphthenates and other oil soluble mono and dicarboxylic acids
23 such as tetrapropyl succinic anhydride. Neutral or highly basic metal salts
24 such as highly basic alkaline earth metal sulfonates (especially calcium and
25 magnesium salts) are frequently used as such detergents. Also useful is
26 nonylphenol sulfide. Similar materials made by reacting an alkylphenol with
27 commercial sulfur dichlorides. Suitable alkylphenol sulfides can also be
28 prepared by reacting alkylphenols with elemental sulfur. Also suitable as
29 detergents are neutral and basic salts of phenols, generally known as
30 phenates, wherein the phenol is generally an alkyl substituted phenolic group,

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1 where the substituent is an aliphatic hydrocarbon group having about 4 to
2 400 carbon atoms.

3

4 Lubricity additives can also be added. Lubricity additives are typically fatty
5 acids and/or fatty esters. Examples of suitable lubricants include polyol esters
6 of C₁₂-C₂₈ acids. The fatty acids are typically used in the concentration range
7 of 10 ppm to 50 ppm, and the esters are typically used in the range of 50 ppm
8 to 250 ppm.

9

10 Some organometallic compounds, for example, barium organometallics, act
11 as combustion catalysts, and can be used as smoke suppressants. Adding
12 these compounds to fuel can reduce the black smoke emissions that result
13 from incomplete combustion. Smoke suppressants based on other metals,
14 e.g., iron, cerium, or platinum, can also be used.

15

16 Anti-foaming additives such as organosilicone compounds can be used,
17 typically at concentrations of 10 ppm or less. Examples of anti-foaming
18 agents include polysiloxanes such as silicone oil and polydimethyl siloxane;
19 acrylate polymers are also suitable.

20

21 Low molecular weight alcohols or glycols can be added to diesel fuel to
22 prevent ice formation.

23

24 Additional additives are used to lower a diesel fuel's pour point (gel point) or
25 cloud point, or improve its cold flow properties. Most of these additives are
26 polymers that interact with the wax crystals that form in diesel fuel when it is
27 cooled below the cloud point.

28

29 Drag reducing additives can also be added to increase the volume of the
30 product that can be delivered. Drag reducing additives are typically used in
31 concentrations below 15 ppm.

32

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1 Antioxidants can be added to the distillate fuel to neutralize or minimize
2 degradation chemistry. Suitable antioxidants include, for example, hindered
3 phenols and certain amines, such as phenylenediamine. They are typically
4 used in the concentration range of 10 ppm to 80 ppm. Examples of
5 antioxidants include those described in U.S. Patent No. 5,200,101, which
6 discloses certain amine/hindered phenol, acid anhydride and thiol ester-
7 derived products.

8

9 Acid-base reactions are another mode of fuel instability. Stabilizers such as
10 strongly basic amines can be added, typically in the concentration range of
11 50 ppm to 150 ppm, to counteract these effects.

12

13 Metal deactivators can be used to tie up (chelate) various metal impurities,
14 neutralizing their catalytic effects on fuel performance. They are typically
15 used in the concentration range of 1 ppm to 15 ppm.

16

17 Multi-component fuel stabilizer packages may contain a dispersant.
18 Dispersants are typically used in the concentration range of 15 ppm to
19 100 ppm.

20

21 Biocides can be used when contamination by microorganisms reaches
22 problem levels. Preferred biocides dissolve in both the fuel and water and
23 can attack the microbes in both phases. Biocides are typically used in the
24 concentration range of 200 ppm to 600 ppm.

25

26 Demulsifiers are surfactants that break up emulsions and allow fuel and water
27 phases to separate. Demulsifiers typically are used in the concentration
28 range of 5 ppm to 30 ppm.

29

30 Dispersants are well known in the lubricating oil field and include high
31 molecular weight alkyl succinimides being the reaction products of oil soluble

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1 polyisobutylene succinic anhydride with ethylene amines such as
2 tetraethylene pentamine and borated salts thereof.

3

4 Corrosion inhibitors are compounds that attach to metal surfaces and form a
5 barrier that prevents attack by corrosive agents. They typically are used in
6 the concentration range of 5 ppm to 15 ppm. Examples of suitable corrosion
7 inhibitors include phosphosulfurized hydrocarbons and the products obtained
8 by reacting a phosphosulfurized hydrocarbon with an alkaline earth metal
9 oxide or hydroxide.

10

11 Examples of oxidation inhibitors include antioxidants such as alkaline earth
12 metal salts of alkylphenol thioesters having preferably C₅-C₁₂ alkyl side chain
13 such as calcium nonylphenol sulfide, barium t-octylphenol sulfide,
14 dioctylphenylamine as well as sulfurized or phosphosulfurized hydrocarbons.
15 Additional examples include oil soluble antioxidant copper compounds such
16 as copper salts of C₁₀₋₁₈ oil soluble fatty acids.

17

18 Examples of friction modifiers include fatty acid esters and amides, glycerol
19 esters of dimerized fatty acids and succinate esters or metal salts thereof.

20

21 Pour point depressants such as C₈₋₁₈ dialkyl fumarate vinyl acetate
22 copolymers, polymethacrylates and wax naphthalene are well known to those
23 of skill in the art.

24 Examples of anti-wear agents include zinc dialkyldithiophosphate, zinc diaryl
25 diphosphate, and sulfurized isobutylene.

26

27 Additional additives are described in U.S. Patent No. 5,898,023 to Francisco
28 et al., the contents of which are hereby incorporated by reference.

29

1 Feedstocks for the Molecular Averaging Reaction

2

3 Examples of preferred feedstocks for the molecular averaging reaction include
4 feedstocks with an average molecular weight of C₂₋₈ (low molecular weight
5 fraction) and C₂₀₊ (high molecular weight fraction). Most preferably, the
6 feedstocks are obtained from Fischer-Tropsch synthesis. However,
7 numerous petroleum feedstocks, for example, those derived from crude oil,
8 are suitable for use. Examples include gas oils and vacuum gas oils,
9 residuum fractions from an atmospheric pressure distillation process,
10 solvent-deasphalted petroleum residues, shale oils, cycle oils, petroleum and
11 slack wax, waxy petroleum feedstocks, NAO wax, and waxes produced in
12 chemical plant processes. Straight chain n-paraffins either alone or with only
13 slightly branched chain paraffins having 20 or more carbon atoms are
14 sometimes referred to herein as waxes.

15

16 Depending on the olefin metathesis catalysts, the feedstocks may need to
17 exclude appreciable amounts of heteroatoms, diolefins, alkynes or saturated
18 C₆ cyclic compounds. If any heteroatoms or saturated C₆ cyclic compounds
19 are present in the feedstock, they may have to be removed before the
20 molecular averaging reaction. Heteroatoms, diolefins and alkynes can be
21 removed by hydrotreating. Saturated cyclic hydrocarbons can be separated
22 from the desired feedstock paraffins by adsorption with molecular sieves or by
23 deoiling or by complexing with urea.

24

25 Preferred petroleum distillates for use in the relatively low molecular weight
26 (C₅₋₆ or less) fraction boil in the normal boiling point range of about 80°C or
27 less. Suitable feedstocks for use in the high molecular weight fraction include
28 any highly paraffinic stream, such as waxes and partially refined waxes (slack
29 waxes). The feedstock may have been subjected to a hydrotreating and/or
30 hydrocracking process before being supplied to the present process.
31 Alternatively, or in addition, the feedstock may be treated in a solvent

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1 extraction process to remove aromatics and sulfur- and nitrogen-containing
2 molecules before being dewaxed.

3 As used herein, the term "waxy petroleum feedstocks" includes petroleum
4 waxes. The feedstock employed in the process of the invention can be a
5 waxy feed which contains greater than about 50% wax, and in some
6 embodiments, even greater than about 90% wax. Such feeds can contain
7 greater than about 70% paraffinic carbon, and in some embodiments, even
8 greater than about 90% paraffinic carbon.

9

10 Examples of additional suitable feeds include waxy distillate stocks such as
11 gas oils, lubricating oil stocks, synthetic oils and waxes such as those
12 produced by Fischer-Tropsch synthesis, high pour point polyalphaolefins,
13 foots oils, synthetic waxes such as normal alpha-olefin waxes, slack waxes,
14 deoiled waxes and microcrystalline waxes. Foots oil is prepared by
15 separating oil from the wax, where the isolated oil is referred to as foots oil.

16

17 Fischer-Tropsch Chemistry

18

19 Preferably, the light gas/naphtha and the wax/heavy fractions are obtained via
20 Fischer-Tropsch chemistry. Fischer-Tropsch chemistry tends to provide a
21 wide range of products from methane and other light hydrocarbons to heavy
22 wax. Syngas is converted to liquid hydrocarbons by contact with a
23 Fischer-Tropsch catalyst under reactive conditions. Depending on the quality
24 of the syngas, it may be desirable to purify the syngas prior to the
25 Fischer-Tropsch reactor to remove carbon dioxide produced during the
26 syngas reaction and any sulfur compounds, if they have not already been
27 removed. This can be accomplished by contacting the syngas with a mildly
28 alkaline solution (e.g., aqueous potassium carbonate) in a packed column.

29

30 In general, Fischer-Tropsch catalysts contain a Group VIII transition metal on
31 a metal oxide support. The catalyst may also contain a noble metal

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1 promoter(s) and/or crystalline molecular sieves. Pragmatically, the two
2 transition metals that are most commonly used in commercial
3 Fischer-Tropsch processes are cobalt or iron. Ruthenium is also an effective
4 Fischer-Tropsch catalyst but is more expensive than cobalt or iron. Where a
5 noble metal is used, platinum and palladium are generally preferred. Suitable
6 metal oxide supports or matrices which can be used include alumina, titania,
7 silica, magnesium oxide, silica-alumina, and the like, and mixtures thereof.

8

9 Although Fischer-Tropsch processes produce a hydrocarbon product having a
10 wide range of molecular sizes, the selectivity of the process toward a given
11 molecular size range as the primary product can be controlled to some extent
12 by the particular catalyst used. In the present process, it is preferred to
13 produce C₂₀-C₅₀ paraffins as the primary product, and therefore, it is preferred
14 to use a cobalt catalyst, although iron catalysts may also be used. One
15 suitable catalyst that can be used is described in U.S. Patent No. 4,579,986
16 as satisfying the relationship:

17

$$18 \quad (3 + 4R) > L/S > (0.3 + 0.4R),$$

19

20 wherein:

21

22 L = the total quantity of cobalt present on the catalyst, expressed as mg
23 Co/ml catalyst,

24 S = the surface area of the catalyst, expressed as m²/ml catalyst, and

25 R = the weight ratio of the quantity of cobalt deposited on the catalyst by
26 kneading to the total quantity of cobalt present on the catalyst.

27

28 Preferably, the catalyst contains about 3-60 ppw cobalt, 0.1-100 ppw of at
29 least one of zirconium, titanium or chromium per 100 ppw of silica, alumina, or
30 silica-alumina and mixtures thereof. Typically, the synthesis gas will contain
31 hydrogen, carbon monoxide and carbon dioxide in a relative mole ratio of
32 about from 0.25 to 2 moles of carbon monoxide and 0.01 to 0.05 moles of

1 carbon dioxide per mole of hydrogen. It is preferred to use a mole ratio of
2 carbon monoxide to hydrogen of about 0.4 to 1, more preferably 0.5 to
3 0.7 moles of carbon monoxide per mole of hydrogen with only minimal
4 amounts of carbon dioxide; preferably less than 0.5 mole percent carbon
5 dioxide.

6

7 The Fischer-Tropsch reaction is typically conducted at temperatures between
8 about 300°F and 700°F (149°C to 371°C), preferably, between about 400°F
9 and 550°F (204°C to 228°C). The pressures are typically between about 10
10 and 500 psia (0.7 to 34 bars), preferably between about 30 and 300 psia (2 to
11 21 bars). The catalyst space velocities are typically between about from 100
12 and 10,000 cc/g/hr., preferably between about 300 and 3,000 cc/g/hr.

13

14 The reaction can be conducted in a variety of reactors for example, fixed bed
15 reactors containing one or more catalyst beds, slurry reactors, fluidized bed
16 reactors, or a combination of different type reactors.

17

18 In a preferred embodiment, the Fischer-Tropsch reaction is conducted in a
19 bubble column slurry reactor. In this type of reactor synthesis gas is bubbled
20 through a slurry that includes catalyst particles in a suspending liquid.

21 Typically, the catalyst has a particle size of between 10 and 110 microns,
22 preferably between 20 and 80 microns, more preferably between 25 and
23 65 microns, and a density of between 0.25 and 0.9 g/cc, preferably between
24 0.3 and 0.75 g/cc. The catalyst typically includes one of the aforementioned
25 catalytic metals, preferably cobalt on one of the aforementioned catalyst
26 supports when formation of C₂₀+ wax fractions is desired. Preferably, such a
27 catalyst comprises about 10 to 14 percent cobalt on a low density fluid
28 support, for example alumina, silica and the like having a density within the
29 ranges set forth above for the catalyst. Since the catalyst metal may be
30 present in the catalyst as oxides, the catalyst is typically reduced with
31 hydrogen prior to contact with the slurry liquid. The starting slurry liquid is

1 typically a heavy hydrocarbon with a viscosity (typically a viscosity between
2 4-100 centistokes at 100°C) sufficient to keep the catalyst particles
3 suspended. The slurry liquid also has a low enough volatility to avoid
4 vaporization during operation (typically an initial boiling point range of
5 between about 350°C and 550°C). The slurry liquid is preferably essentially
6 free of contaminants such as sulfur, phosphorous or chlorine compounds.
7 Initially, it may be desirable to use a synthetic hydrocarbon fluid such as a
8 synthetic olefin oligomer as the slurry fluid.

9

10 The slurry typically has a catalyst concentration of between about 2 and
11 40 percent catalyst, preferably between about 5 and 20 percent, and more
12 preferably between about 7 and 15 percent catalyst based on the total weight
13 of the catalyst, i.e., metal plus support. The syngas feed typically has a
14 hydrogen to carbon monoxide mole ratio of between about 0.5 and 4 moles of
15 hydrogen per mole of carbon monoxide, preferably between about 1 and
16 2.5 moles, and more preferably between about 1.5 and 2 moles.

17

18 The bubble slurry reactor is typically operated at temperatures within the
19 range of between about 150°C and 300°C, preferably between about 185°C
20 and 265°C, and more preferably between about 210°C and 230°C. The
21 pressures are within the range of between about 1 and 70 bar, preferably
22 between about 6 and 35 bar, and most preferably between about 10 and
23 30 bar (1 bar = 14.5 psia). Typical synthesis gas linear velocity ranges in the
24 reactor are from about 2 to 40 cm per sec., preferably from about 6 to 10 cm
25 per sec. Additional details regarding bubble column slurry reactors can be
26 found, for example, in Y. T. Shah et al., "Design Parameters Estimations for
27 Bubble Column Reactors", *AIChE Journal*, 28 No. 3, pp. 353-379 (May 1982);
28 Ramachandran et al., "Bubble Column Slurry Reactor, Three-Phase Catalytic
29 Reactors", Chapter 10, pp. 308-332, Gordon and Broch Science Publishers
30 (1983); Deckwer et al., "Modeling the Fischer-Tropsch Synthesis in the Slurry
31 Phase", *Ind. Eng. Chem. Process Des. Dev.*, v 21, No. 2, pp. 231-241 (1982);

1 Kölbel et al., "The Fischer-Tropsch Synthesis in the Liquid Phase", *Catal.*
2 *Rev.-Sci. Eng.*, v. 21(n), pp. 225-274 (1980); and U.S. Patent No. 5,348,982,
3 the contents of each of which are hereby incorporated by reference in their
4 entirety.

5

6 The relatively high (for example, C₂₀+) and relatively low (for example, C₂₋₆)
7 molecular weight fractions which are to be molecularly averaged are
8 described herein in terms of a Fischer-Tropsch reaction product. However,
9 these fractions can also be obtained through various modifications of the
10 literal Fischer-Tropsch process by which hydrogen (or water) and carbon
11 monoxide (or carbon dioxide) are converted to hydrocarbons (e.g., paraffins,
12 ethers, etc.) and to the products of such processes. Thus, the term
13 Fischer-Tropsch type product or process is intended to apply to
14 Fischer-Tropsch processes and products and the various modifications
15 thereof and the products thereof. For example, the term is intended to apply
16 to the Kolbel-Engelhardt process typically described by the reaction:

17 $3\text{CO} + \text{H}_2\text{O} \rightarrow \text{---CH}_2\text{---} + 2\text{CO}_2$

18

19 The molecular averaging process described combines a low molecular weight
20 olefinic fraction (C₂₋₆, light gas/naphtha) and a high molecular weight fraction
21 (C₂₀₊, wax/heavy fraction) which is dehydrogenated to form a high molecular
22 weight olefinic fraction prior to molecular averaging.

23

24 The two fractions can be obtained in separate Fischer-Tropsch reactions.

25 The low molecular weight fraction can be obtained using conditions in which

26 chain growth probabilities are relatively low to moderate, and the product of

27 the reaction includes a relatively high proportion of low molecular weight (C_{2-8})

28 olefins and a relatively low proportion of high molecular weight (C_{30+}) waxes.

29 The high molecular weight fraction can be obtained using conditions in which

30 chain growth probabilities are relatively high, and the product of the reaction

31 includes a relatively low proportion of low molecular weight (C_{2-8}) olefins and a

1 relatively high proportion of high molecular weight (C₃₀₊) waxes. After the
2 wax product is dehydrogenated, it can be combined with the product of the
3 first Fischer-Tropsch reaction for molecular averaging.

4

5 Suitable catalysts, supports and promoters for separately forming the low and
6 high molecular weight fractions are described in detail below.

7

8 Catalysts with low chain growth probabilities

9

10 Suitable catalysts that provide relatively low (alpha values of between 0.600
11 and 0.700) to moderate (alpha values of between 0.700 and 0.800) chain
12 growth probabilities tend to provide high yields of light (C₂₋₈) alpha olefins.
13 Such catalysts are well known to those of skill in the art. Preferably, the
14 catalyst used in the first stage is an iron-containing catalyst. Iron itself can be
15 used and, when iron oxides are formed, can be reduced with hydrogen back
16 to iron. However, because the presence of iron fines in the product stream is
17 not preferred, and because iron oxides (rust) decrease the surface area of the
18 catalyst available for reaction, other iron-containing catalysts are preferred.

19 Examples of suitable iron-containing catalysts include those described in U.S.
20 Patent No. 4,544,674 to Fiato et al.

21

22 In a preferred embodiment, the iron catalysts include at least about 10 to
23 about 60 weight percent iron. More preferably, they include between about 20
24 to about 60 weight percent iron, and most preferably about 30 to about
25 50 weight percent iron. These catalysts can be unsupported, but are
26 preferably promoted with a refractory metal oxide (SiO₂, Al₂O₃, etc.), alkali (K,
27 Na, Rb) and/or Group IB metals (Cu, Ag). These catalysts are usually
28 calcined, but usually not reduced, rather they are brought up to reaction
29 temperature directly in the CO/H₂ feed.

30

31 Co-precipitated iron-based catalysts, including those containing cobalt, can be
32 used. High levels of cobalt in an iron-cobalt alloy are known to produce

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1 enhanced selectivity to olefinic products, as described in Stud. Surf. Sci. Catal. 7, Pt/A, pg. 432 (1981).

3

4 Examples of co-precipitated iron-cobalt catalysts and/or alloys include those
5 described in U.S. Patent Nos. 2,850,515, 2,686,195, 2,662,090, and
6 2,735,862; *AICHE 1981 Summer Nat'l Meeting Preprint No. 408, "The*
7 *Synthesis of Light Hydrocarbons from CO and H₂ Mixtures over Selected*
8 *Metal Catalysts"* ACS 173rd Symposium, Fuel Division, New Orleans, March
9 1977; *J. Catalysis* 1981, No. 72(1), pp. 37-50; *Adv. Chem. Ser.* 1981, 194,
10 573-88; *Physics Reports* (Section C of Physics Letters) 12 No. 5 (1974)
11 pp. 335-374; UK patent application No. 2050859A; *J. Catalysis* 72, 95-110
12 (1981); Gmelins Handbuch der Anorganische Chemie 8, *Auflage* (1959),
13 pg. 59; *Hydrocarbon Processing*, May 1983, pp. 88-96; and *Chem. Ing. Tech.*
14 49 (1977) No. 6, pp. 463-468.

15

16 Methods for producing high surface area metal oxides are described, for
17 example, in the French article, "C. R. Acad. Sc. Paris", p. 268 (28 May 1969)
18 by P. Courte and B. Delmon. Metal oxides with a high surface area are
19 prepared by evaporating to dryness aqueous solutions of the corresponding
20 glycolic acid, lactic acid, malic or tartaric acid metal salts. One oxide that was
21 prepared was CoFe₂O₄.

22

23 Iron-cobalt spinels which contain low levels of cobalt, in an iron/cobalt atomic
24 ratio of 7:1 to 35:1, are converted to Fischer-Tropsch catalysts upon reduction
25 and carbiding (see, for example, U.S. Patent No. 4,544,674 to Fiato et al.).
26 These catalysts tend to exhibit high activity and selectivity to C₂-C₆ olefins and
27 low methane production.

28

29 Catalysts with high chain growth probabilities

30

31 Catalysts that provide relatively high chain growth probabilities (alpha values
32 of between 0.800 and 0.900) can be used to form a product that mostly

-20-

1 includes C₂₀+ waxes. Any catalyst that provides relatively high chain growth
2 probabilities can be used. Preferably, the catalyst used in the second stage is
3 a cobalt-containing catalyst. Ruthenium is also an effective Fischer-Tropsch
4 catalyst but is more expensive.

5

6 One suitable cobalt catalyst that can be used is described in U.S. Patent
7 No. 4,579,986, as satisfying the relationship:

8

$$9 \quad (3 + 4R) > L/S > (0.3 + 0.4R),$$

10

11 wherein:

12

13 L = the total quantity of cobalt present on the catalyst, expressed as
14 mg Co/ml catalyst;

15 S = the surface area of the catalyst, expressed as m²/ml catalyst; and

16 R = the weight ratio of the quantity of cobalt deposited on the catalyst
17 by kneading to the total quantity of cobalt present on the catalyst.

18

19 Other suitable catalysts include those described in U.S. Patent
20 Nos. 4,077,995, 4,039,302, 4,151,190, 4,088,671, 4,042,614 and 4,171,320.
21 U.S. Patent No. 4,077,995 discloses a catalyst that includes a sulfided mixture
22 of CoO, Al₂O₃ and ZnO. U.S. Patent No. 4,039,302 discloses a mixture of the
23 oxides of Co, Al, Zn and Mo. U.S. Patent No. 4,151,190 discloses a metal
24 oxide or sulfide of Mo, W, Re, Ru, Ni or Pt, plus an alkali or alkaline earth
25 metal, with Mo-K on carbon being preferred.

26

27 U.S. Patent No. 4,088,671 discloses minimizing methane production by using
28 a small amount of Ru on a cobalt catalyst. Examples of supported ruthenium
29 catalysts suitable for hydrocarbon synthesis via Fischer-Tropsch reactions are
30 disclosed, for example, in U.S. Patent Nos. 4,042,614 and 4,171,320.

31

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1 In general, the amount of cobalt catalytic metal present is about 1 to about
2 50 weight percent of the total catalyst composition, more preferably from
3 about 10.0 to about 25 weight percent.

4

5 Preferably, the catalyst which provides high chain growth probabilities
6 contains about 3-60 ppw cobalt, 0.1-100 ppw of at least one of zirconium,
7 titanium or chromium per 100 ppw of silica, alumina, or silica-alumina and
8 mixtures thereof.

9

10 Catalyst Supports

11

12 The type of support used can influence methane production, which should be
13 minimized regardless of whether the catalyst used promotes high or low chain
14 growth probabilities. Suitable metal oxide supports or matrices which can be
15 used to minimize methane production include alumina, titania, silica,
16 magnesium oxide, silica-alumina, and the like; and mixtures thereof.

17 Examples include titania, zirconium titanate, mixtures of titania and alumina,
18 mixtures of titania and silica, alkaline earth titanates, alkali titanates, rare
19 earth titanates and mixtures of any one of the foregoing with supports
20 selected from the group consisting of vanadia, niobia, tantalum, alumina, silica
21 and mixtures thereof.

22

23 In the case of supported ruthenium catalysts, the use of a titania or titania-
24 containing support will result in lower methane production than, for example, a
25 silica, alumina or manganese oxide support. Accordingly, titania and titania-
26 containing supports are preferred.

27

28 Typically, the catalysts have a particle size of between 10 and 110 microns,
29 preferably between 20 and 80 microns, more preferably between 25 and
30 65 microns, and have a density of between 0.25 and 0.9 g/cc, preferably
31 between 0.3 and 0.75 g/cc. The catalysts typically include one of the above-
32 mentioned catalytic metals, preferably including iron for low molecular weight

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1 olefin production and cobalt for C₂₀+ wax production, on one of the above-
2 mentioned catalyst supports. Preferably, the cobalt-containing catalysts
3 include about 10 to 14 percent cobalt on a low density fluid support, for
4 example, alumina, silica and the like, having a density within the ranges set
5 forth above for the catalyst.

6

7 Promoters and Noble Metals

8

9 Methane selectivity is also influenced by the choice of promoter. Alkali metal
10 promoters are known for reducing the methane selectivities of iron catalysts.
11 Noble metals, such as ruthenium, supported on inorganic refractory oxide
12 supports, exhibit superior hydrocarbon synthesis characteristics with relatively
13 low methane production. Where a noble metal is used, platinum and
14 palladium are generally preferred. Accordingly, alkali metal promoters and/or
15 noble metals can be included in the catalyst bed of the first stage provided
16 that they do not significantly alter the reaction kinetics from slow chain growth
17 probabilities to fast chain growth probabilities.

18

19 The disclosures of each of the patents discussed above are incorporated
20 herein by reference in their entirety.

21

22 The Separation of Product From the Fischer-Tropsch Reaction

23

24 The products from Fischer-Tropsch reactions generally include a gaseous
25 reaction product and a liquid reaction product. The gaseous reaction product
26 includes hydrocarbons boiling below about 650°F (e.g., tail gases through
27 middle distillates). The liquid reaction product (the condensate fraction)
28 includes hydrocarbons boiling above about 650°F (e.g., vacuum gas oil
29 through heavy paraffins).

30

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1 The minus 650°F product can be separated into a tail gas fraction and a
2 condensate fraction, i.e., about C₅ to C₂₀ normal paraffins and higher boiling
3 hydrocarbons, using, for example, a high pressure and/or lower temperature
4 vapor-liquid separator or low pressure separators or a combination of
5 separators. The preferred fractions for preparing the distillate fuel
6 composition via molecular averaging generally include C₂₋₅ and C₂₀₊ paraffins
7 and olefins.

8

9 After removing the particulate catalyst, the fraction boiling above about 650°F
10 (the condensate fraction) can be separated into a wax fraction boiling in the
11 range of about 650°F-1200°F, primarily about containing C₂₀ to C₅₀ linear
12 paraffins with relatively small amounts of higher boiling branched paraffins,
13 and one or more fractions boiling above about 1200°F. However, both
14 fractions are preferably combined for molecular averaging.

15

16 Products in the desired range (for example, C₅₋₂₀, preferably around C₈₋₁₂) are
17 preferably isolated and used directly to prepare distillate fuel compositions.

18 Products in the relatively low molecular weight fraction (for example, C₂₋₆, light
19 gas/naphtha) and the relatively high molecular weight fraction (for example,
20 C₂₀₊, wax/heavy fractions) can be isolated and combined for molecular
21 redistribution/averaging to arrive at a desired fraction. The product of the
22 molecular averaging reaction can be distilled to provide a desired C₅₋₂₀
23 fraction, and also relatively low and high molecular weight fractions, which can
24 be reprocessed in the molecular averaging stage.

25

26 More product in the desired range is produced when the reactants have
27 molecular weights closer to the target molecular weight. Of course, following
28 fractional distillation and isolation of the product of the molecular averaging
29 reaction, the other fractions can be isolated and re-subjected to molecular
30 averaging conditions.

31

1 Hydrotreating and/or Hydrocracking Chemistry

2

3 Fractions used in the molecular averaging chemistry may include heteroatoms
4 such as sulfur or nitrogen, diolefins and alkynes that may adversely affect the
5 catalysts used in the molecular averaging reaction. If sulfur impurities are
6 present in the starting materials, they can be removed using means well
7 known to those of skill in the art, for example, extractive Merox, hydrotreating,
8 adsorption, etc. Nitrogen-containing impurities can also be removed using
9 means well known to those of skill in the art. Hydrotreating and hydrocracking
10 are preferred means for removing these and other impurities from the heavy
11 wax feed component. Removal of these components from the light naphtha
12 and gas streams must use techniques that minimize the saturation of the
13 olefins in these streams. Extractive Merox is suitable for removing sulfur
14 compounds and acids from the light streams. The other compounds can be
15 removed, for example, by adsorption, dehydration of alcohols, and selective
16 hydrogenation. Selective hydrogenation of diolefins, for example, is well
17 known in the art. One example of a selective hydrogenation of diolefins in the
18 presence of olefins is UOP's DeFine process.

19

20 Accordingly, it is preferred that the heavy wax fractions be hydrotreated
21 and/or hydrocracked to remove the heteroatoms before performing the
22 molecular averaging process described herein. Hydrogenation catalysts can
23 be used to hydrotreat the products resulting from the Fischer-Tropsch,
24 molecular averaging and/or isomerization reactions, although it is preferred
25 not to hydrotreat the products from the Fischer-Tropsch reaction, since the
26 olefins necessary for the molecular averaging step would be hydrogenated.

27

28 As used herein, the terms "hydrotreating" and "hydrocracking" are given their
29 conventional meaning and describe processes that are well known to those
30 skilled in the art. Hydrotreating refers to a catalytic process, usually carried
31 out in the presence of free hydrogen, in which the primary purpose is the
32 desulfurization and/or denitration of the feedstock. Generally, in

1 hydrotreating operations, cracking of the hydrocarbon molecules, i.e.,
2 breaking the larger hydrocarbon molecules into smaller hydrocarbon
3 molecules, is minimized and the unsaturated hydrocarbons are either fully or
4 partially hydrogenated.

5

6 Hydrocracking refers to a catalytic process, usually carried out in the
7 presence of free hydrogen, in which the cracking of the larger hydrocarbon
8 molecules is a primary purpose of the operation. Desulfurization and/or
9 denitrification of the feed stock usually will also occur.

10

11 Catalysts used in carrying out hydrotreating and hydrocracking operations are
12 well known in the art. See, for example, U.S. Patent Nos. 4,347,121 and
13 4,810,357 for general descriptions of hydrotreating, hydrocracking, and typical
14 catalysts used in each process.

15

16 Suitable catalysts include noble metals from Group VIIA, such as platinum or
17 palladium on an alumina or siliceous matrix, and unsulfided Group VIIA and
18 Group VIB, such as nickel-molybdenum or nickel-tin on an alumina or
19 siliceous matrix. U.S. Pat. No. 3,852,207 describes suitable noble metal
20 catalysts and mild hydrotreating conditions. Other suitable catalysts are
21 described, for example, in U.S. Patent Nos. 4,157,294 and 3,904,513. The
22 non-noble metal (such as nickel-molybdenum) hydrogenation metal are
23 usually present in the final catalyst composition as oxides, or more preferably
24 or possibly, as sulfides when such compounds are readily formed from the
25 particular metal involved. Preferred non-noble metal catalyst compositions
26 contain in excess of about 5 weight percent, preferably about 5 to about
27 40 weight percent molybdenum and/or tungsten, and at least about 0.5, and
28 generally about 1 to about 15 weight percent of nickel and/or cobalt
29 determined as the corresponding oxides. The noble metal (such as platinum)
30 catalyst contains in excess of 0.01 percent metal, preferably between 0.1 and
31 1.0 percent metal. Combinations of noble metals may also be used, such as
32 mixtures of platinum and palladium.

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1 The hydrogenation components can be incorporated into the overall catalyst
2 composition by any one of numerous procedures. The hydrogenation
3 components can be added to matrix component by co-mulling, impregnation,
4 or ion exchange and the Group VI components, i.e., molybdenum and
5 tungsten can be combined with the refractory oxide by impregnation,
6 co-mulling or co-precipitation. Although these components can be combined
7 with the catalyst matrix as the sulfides, that may not be preferred, as the sulfur
8 compounds may interfere with some molecular averaging or Fischer-Tropsch
9 catalysts.

10

11 The matrix component can be of many types including some that have acidic
12 catalytic activity. Ones that have activity include amorphous silica-alumina or
13 may be a zeolitic or non-zeolitic crystalline molecular sieve. Examples of
14 suitable matrix molecular sieves include zeolite Y, zeolite X and the so-called
15 ultra stable zeolite Y and high structural silica:alumina ratio zeolite Y such as
16 that described in U.S. Patent Nos. 4,401,556, 4,820,402 and 5,059,567.
17 Small crystal size zeolite Y, such as that described in U.S. Patent
18 No. 5,073,530, can also be used. Non-zeolitic molecular sieves which can be
19 used include, for example, silicoaluminophosphates (SAPO),
20 ferroaluminophosphate, titanium aluminophosphate, and the various ELAPO
21 molecular sieves described in U.S. Patent No. 4,913,799 and the references
22 cited therein. Details regarding the preparation of various non-zeolite
23 molecular sieves can be found in U.S. Patent Nos. 5,114,563 (SAPO);
24 4,913,799 and the various references cited in U.S. Patent No. 4,913,799.
25 Mesoporous molecular sieves can also be used, for example, the M41S family
26 of materials (*J. Am. Chem. Soc.* 1992, 114, 10834-10843), MCM-41 (U.S.
27 Patent Nos. 5,246, 689, 5,198,203 and 5,334,368), and MCM-48 (Kresge
28 et al., *Nature* 359 (1992) 710).

29

30 Suitable matrix materials may also include synthetic or natural substances as
31 well as inorganic materials such as clay, silica and/or metal oxides such as
32 silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-berylia,

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1 silica-titania as well as ternary compositions, such as silica-alumina-thoria,
2 silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia zirconia.
3 The latter may be either naturally occurring or in the form of gelatinous
4 precipitates or gels including mixtures of silica and metal oxides. Naturally
5 occurring clays which can be composited with the catalyst include those of the
6 montmorillonite and kaolin families. These clays can be used in the raw state
7 as originally mined or initially subjected to calcination, acid treatment or
8 chemical modification.

9
10 Furthermore, more than one catalyst type may be used in the reactor. The
11 different catalyst types can be separated into layers or mixed. Typical
12 hydrotreating conditions vary over a wide range. In general, the overall LHSV
13 is about 0.25 to 2.0, preferably about 0.5 to 1.0. The hydrogen partial
14 pressure is greater than 200 psia, preferably ranging from about 500 psia to
15 about 2000 psia. Hydrogen recirculation rates are typically greater than
16 50 SCF/Bbl, and are preferably between 1000 and 5000 SCF/Bbl.
17 Temperatures range from about 300°F to about 750°F, preferably ranging
18 from 450°F to 600°F.

19
20 The contents of each of the patents and publications referred to above are
21 hereby incorporated by reference in its entirety.

22
23 Molecular Redistribution/Averaging
24
25 As used herein, "molecular redistribution" is a process in which a mixture of
26 olefins with a relatively wide size distribution is converted into an olefin stream
27 with a relatively narrow size distribution. The terms "molecular averaging" and
28 "disproportionation" are also used herein to describe molecular averaging.
29

1 In the process described herein, a high molecular weight wax fraction is
2 partially dehydrogenated and combined with low molecular weight olefins.
3 The combined olefins are then subjected to olefin metathesis conditions.
4
5 A typical dehydrogenation/hydrogenation catalyst includes a platinum
6 component and a typical metathesis catalyst includes a tungsten component.
7 Examples of suitable catalysts are described in U.S. Patent No. 3,856,876,
8 the entire disclosure of which is herein incorporated by reference. The
9 individual steps in the overall molecular averaging reaction are discussed in
10 detail below.

11

12 Dehydrogenation

13

14 The catalyst used to dehydrogenate the relatively high molecular weight
15 paraffin fraction must have dehydrogenation activity. It is necessary to
16 convert at least a portion of the paraffins in the relatively high molecular
17 weight feed to olefins, which are believed to be the actual species that
18 undergo olefin metathesis.

19

20 Platinum and palladium or the compounds thereof are preferred for inclusion
21 in the dehydrogenation/hydrogenation component, with platinum or a
22 compound thereof being especially preferred. As noted previously, when
23 referring to a particular metal in this disclosure as being useful in the present
24 invention, the metal may be present as elemental metal or as a compound of
25 the metal. As discussed above, reference to a particular metal in this
26 disclosure is not intended to limit the invention to any particular form of the
27 metal unless the specific name of the compound is given, as in the examples
28 in which specific compounds are named as being used in the preparations.

29

30 The dehydrogenation step can be conducted by passing the linear paraffin
31 feed over a dehydrogenation catalyst under dehydrogenating reaction
32 conditions. The dehydrogenation is typically conducted in the presence of

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1 hydrogen and correspondingly a certain percentage of oxygenates, e.g., linear
2 alcohols, will be hydrogenated to the corresponding paraffins and then
3 dehydrogenated to the corresponding internal olefins. Thus, the linear
4 hydrocarbon feed may contain a substantial amount of linear oxygenates. On
5 a mole percent basis, this may be up to about 50 mol.% linear oxygenates
6 although it is preferably less than 30 mol.%. On a weight percent basis of
7 oxygen, this will generally be much less, because the linear hydrocarbons are
8 typically made up of only one or two oxygen atoms per molecule.

9

10 In order to reduce or eliminate the amount of diolefins produced or other
11 undesired by-products, the reaction conversion to internal olefins should
12 preferably not exceed 50% and more preferably should not exceed 30%
13 based on the linear hydrocarbon content of the feed. Preferably, the minimum
14 conversion should be at least 15 wt. % and more preferably at least 20 wt. %.

15

16 Because of the low dehydrogenation conversions, feedstocks with a higher
17 proportion of linear hydrocarbons having carbon atom numbers in the upper
18 range of the desired normal alpha olefin (NAO) products are preferred to
19 facilitate separation of the desired NAO's based on boiling point differences
20 between the NAO and unreacted paraffins. Preferably, the final carbon
21 numbers in the NAO product are within 50 carbon atoms of the initial carbon
22 numbers in the linear paraffinic hydrocarbon feed. More preferably, the final
23 carbon numbers are within 25 carbon atoms, and most preferably within
24 10 carbon atoms.

25

26 The dehydrogenation is typically conducted at temperatures between about
27 500°F and 1000°F (260°C and 538°C), preferably between about 600°F and
28 800°F (316°C and 427°C). The pressures are preferably between about 0.1
29 and 10 atms, more preferably between about 0.5 and 4 atms absolute
30 pressure (about 0.5 to 4 bars). The LHSV (liquid hourly space velocity) is

1 preferably between about 1 and 50 hr⁻¹, preferably between about 20 and
2 40 hr⁻¹. The products generally and preferably include internal olefins.

3

4 Since longer chained paraffins are more easy to dehydrogenate than shorter
5 chained paraffins, more rigorous conditions, e.g., higher temperatures and/or
6 lower space velocities, within these ranges are typically used where shorter
7 chain paraffins are dehydrogenated. Conversely, lower temperatures and/or
8 higher space velocities, within these ranges, are typically used where longer
9 chained paraffins are dehydrogenated. The dehydrogenation is also typically
10 conducted in the presence of a gaseous diluent, typically and preferably
11 hydrogen. Although hydrogen is the preferred diluent, other art-recognized
12 diluents may also be used, either individually or in admixture with hydrogen or
13 each other, such as steam, methane, ethane, carbon dioxide, and the like.
14 Hydrogen is preferred because it serves the dual-function of not only lowering
15 the partial pressure of the dehydrogenatable hydrocarbon, but also of
16 suppressing the formation of hydrogen-deficient, carbonaceous deposits on
17 the catalytic composite. Hydrogen is typically used in amounts sufficient to
18 insure a hydrogen to hydrocarbon feed mole ratio of about from 2:1 to 40:1,
19 preferably in the range of about from 5:1 to 20:1.

20

21 Suitable dehydrogenation catalysts which can be used include Group VIII
22 noble metals, e.g., iron, cobalt, nickel, palladium, platinum, rhodium,
23 ruthenium, osmium, and iridium, preferably on an oxide support.

24

25 Less desirably, combinations of Group VIII non-noble and Group VIB metals
26 or their oxides, e.g., chromium oxide, may also be used. Suitable catalyst
27 supports include, for example, silica, silicalite, zeolites, molecular sieves,
28 activated carbon alumina, silica-alumina, silica-magnesia, silica-thoria, silica-
29 berylia, silica-titania, silica-aluminum-thoria, silica-alumina-zirconia kaolin
30 clays, montmorillonite clays and the like. In general, platinum on alumina or
31 silicalite afford very good results in this reaction. Typically, the catalyst
32 contains about from 0.01 to 5 wt. %, preferably 0.1 to 1 wt. % of the

1 dehydrogenation metal (e.g., platinum). Combination metal catalysts such as
2 those described in U.S. Patent Nos. 4,013,733; 4,101,593 and 4,148,833, the
3 contents of which are hereby incorporated by reference in their entirety, can
4 also be used.

5

6 Preferably, hydrogen and any light gases, such as water vapor formed by the
7 hydrogenation of oxygenates, or hydrogen sulfide formed by the
8 hydrogenation of organic sulfur are removed from the reaction product prior to
9 olefin metathesis, for example, by using one or more vapor/liquid separators.
10 In general, where the feedstock is hydrotreated prior to the dehydrogenation,
11 these gases will be removed by gas/liquid phase separation following the
12 hydrotreatment. Since dehydrogenation produces a net gain in hydrogen, the
13 hydrogen may be taken off for other plant uses or as is typically the case,
14 where the dehydrogenation is conducted in the presence of hydrogen, a
15 portion of the recovered hydrogen can be recycled back to the
16 dehydrogenation reactor. Further information regarding dehydrogenation and
17 dehydrogenation catalysts can, for example, be found in U.S. Patents
18 Nos. 4,046,715; 4,101,593; and 4,124,649, the contents of which are hereby
19 incorporated by reference in their entirety. A variety of commercial processes
20 also incorporate dehydrogenation processes, in their overall process scheme,
21 which dehydrogenation processes may also be used in the present process to
22 dehydrogen the paraffinic hydrocarbons. Examples of such processes
23 include the dehydrogenation process portion of the Pacol process for
24 manufacturing linear alkylbenzenes, described in Vora et al., Chemistry and
25 Industry, 187-191 (1990); Schulz R. C. et al., Second World Conference on
26 Detergents, Montreaux, Switzerland (October 1986); and Vora et al., Second
27 World Surfactants Congress, Paris France (May 1988), hereby incorporated
28 by reference in their entirety.

29

30 If desired, diolefins produced during the dehydrogenation step may be
31 removed by known adsorption processes or selective hydrogenation
32 processes which selectively hydrogenate diolefins to monoolefins without

1 significantly hydrogenating monoolefins. One such selective hydrogenation
2 process known as the DeFine process is described in the Vora et al.
3 Chemistry and Industry publication cited above. If desired, branched
4 hydrocarbons may be removed before or after the dehydrogenation process
5 or after the olefin metathesis process described below by any suitable
6 process, typically by adsorption. One commercial adsorption process for
7 removing branched hydrocarbons and aromatics from linear paraffins is
8 known as the Molex or Sorbex process described in McPhee, Petroleum
9 Technology Quarterly, pages 127-131, (Winter 1999/2000) which description
10 is hereby incorporated by reference.

11

12 Olefin Metathesis

13

14 The relatively low molecular weight fractions (i.e., C₂₋₆) and relatively high
15 molecular weight fraction (i.e., at or above C₂₀) are metathesized to form a
16 desired fraction (i.e., around C₅₋₂₀). This involves using an appropriate olefin
17 metathesis catalyst under conditions selected to convert a significant portion
18 of the relatively high molecular weight and relatively low molecular weight
19 fractions to a desired fraction.

20

21 The low molecular weight olefin fraction can be used directly in the olefin
22 metathesis reaction. As discussed above, at least a portion of the relatively
23 high molecular weight waxy fraction must be converted into olefins in a
24 process known as dehydrogenation or unsaturation before it can participate in
25 the reaction. The resulting olefins are combined with the low molecular
26 weight olefins and the reaction mixture is subjected to olefin metathesis
27 conditions. The metathesized olefins are then optionally converted into
28 paraffins in a process known as hydrogenation or saturation, although they
29 can be used in distillate fuel compositions without first having been
30 hydrogenated.

31

1 Various catalysts are known to catalyze the olefin metathesis reaction. The
2 catalyst mass used in the olefin metathesis reaction must have olefin
3 metathesis activity. Olefin metathesis typically uses conventional catalysts,
4 such as W/SiO₂ (or inexpensive variations). Usually, the olefin metathesis
5 catalyst will include one or more of a metal or the compound of a metal from
6 Group VIB or Group VIIIB of the Periodic Table of the Elements, which include
7 chromium, manganese, molybdenum, rhenium and tungsten. Preferred for
8 inclusion in the olefin metathesis component are molybdenum, rhenium,
9 tungsten, and the compounds thereof. Particularly preferred for use in the
10 olefin metathesis component is tungsten or a compound thereof. As
11 discussed, the metals described above may be present as elemental metals
12 or as compounds of the metals, such as, for example, as an oxide of the
13 metal. It is also understood that the metals may be present on the catalyst
14 component either alone or in combination with other metals.

15
16 The chemistry does not require using hydrogen gas, and therefore does not
17 require relatively expensive recycle gas compressors. The chemistry is
18 typically performed at mild pressures (100-5000 psig). The chemistry is
19 typically thermoneutral and, therefore, there is no need for additional
20 equipment to control the temperature.

21
22 Depending on the nature of the catalysts, olefin metathesis (and
23 dehydrogenation) may be sensitive to impurities in the feedstock, such as
24 sulfur- and nitrogen-containing compounds and moisture, and these must be
25 removed prior to the reaction. Typically, if the paraffins being metathesized
26 result from a Fischer-Tropsch reaction, they do not include an appreciable
27 amount of sulfur. However, if the paraffins resulted from another process, for
28 example, distillation of crude oil, they may contain sufficient sulfur impurities
29 to adversely effect the olefin metathesis chemistry.

30
31 The presence of excess hydrogen in the olefin metathesis zone can effect the
32 equilibrium of the olefin metathesis reaction and to deactivate the catalyst.

1 Since the composition of the fractions may vary, some routine
2 experimentation will be necessary to identify the contaminants that are
3 present and identify the optimal processing scheme and catalyst to use in
4 carrying out the invention.

5

6 The process conditions selected for carrying out the olefin metathesis step will
7 depend upon the olefin metathesis catalyst used. In general, the temperature
8 in the reaction zone will be within the range of from about 400°F (200°C) to
9 about 1000°F (540°C), with temperatures in the range of from about 500°F
10 (260°C) to about 850°F (455°C) usually being preferred. In general, the
11 conversion of the olefins by olefin metathesis increases with an increase in
12 pressure. Therefore, the selection of the optimal pressure for carrying out the
13 process will usually be at the highest practical pressure under the
14 circumstances. Accordingly, the pressure in the reaction zone should be
15 maintained above 100 psig, and preferably the pressure should be maintained
16 above 500 psig. The maximum practical pressure for the practice of the
17 invention is about 5000 psig. More typically, the practical operating pressure
18 will below about 3000 psig. The feedstock to the olefin metathesis reactor
19 should contain a minimum of olefins, and preferably should contain no added
20 hydrogen.

21

22 Saturated and partially saturated cyclic hydrocarbons (cycloparaffins,
23 aromatic-cycloparaffins, and alkyl derivatives of these species) can form
24 hydrogen during the molecular averaging reaction. This hydrogen can inhibit
25 the reaction, thus these species should be substantially excluded from the
26 feed. The desired paraffins can be separated from the saturated and partially
27 saturated cyclic hydrocarbons by deoiling or by use of molecular sieve
28 adsorbents, or by deoiling or by extraction with urea. These techniques are
29 well known in the industry. Separation with urea is described by Hepp, Box
30 and Ray in Ind. Eng. Chem., 45: 112 (1953). Fully aromatic cyclic
31 hydrocarbons do not form hydrogen and can be tolerated. Polycyclic

1 aromatics can form carbon deposits, and these species should also be
2 substantially excluded from the feed. This can be done by use of
3 hydrotreating and hydrocracking.

4

5 Tungsten catalysts are particularly preferred for carrying out the molecular
6 averaging step, because the molecular averaging reaction will proceed under
7 relatively mild conditions. When using the tungsten catalysts, the temperature
8 should be maintained within the range of from about 400°F (200°C) to about
9 1000°F (540°C), with temperatures above about 500°F (260°C) and below
10 about 800°F being particularly desirable.

11

12 The olefin metathesis reaction described above is reversible, which means
13 that the reaction proceeds toward a roughly thermodynamic equilibrium limit.
14 Therefore, since the feed to the olefin metathesis zone has two streams of
15 paraffins at different molecular weights, equilibrium will drive the reaction to
16 produce a product stream having a molecular weight between that of the two
17 streams. The zone in which the olefin metathesis occurs is referred to herein
18 as an olefin metathesis zone. It is desirable to reduce the concentration of the
19 desired products in the olefin metathesis zone to as low a concentration as
20 possible to favor the reactions in the desired direction. As such, some routine
21 experimentation may be necessary to find the optimal conditions for
22 conducting the process.

23

24 In the event the catalyst deactivates with the time-on-stream, specific
25 processes that are well known to those skilled in art are available for the
26 regeneration of the catalysts.

27

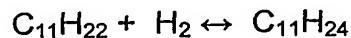
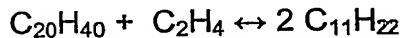
28 Any number of reactors can be used, such as fixed bed, fluidized bed,
29 ebulated bed, and the like. An example of a suitable reactor is a catalytic
30 distillation reactor.

31

1 When the relatively high molecular weight and relatively low molecular weight
2 fractions are combined, it may be advantageous to take representative
3 samples of each fraction and subject them to olefin metathesis, while
4 adjusting the relative amounts of the fractions until a product with desired
5 properties is obtained. Then, the reaction can be scaled up using the relative
6 ratios of each of the fractions that resulted in the desired product. Using this
7 method, one can "dial in" a molecular weight distribution which can be roughly
8 controlled. This can take and result in a reasonably consistent product.

10 Following olefin metathesis, the olefins are optionally converted back into
11 paraffins using a hydrogenation catalyst and hydrogen. While it is not
12 intended that the present invention be limited to any particular mechanism, it
13 may be helpful in explaining the choice of catalysts to further discuss the
14 sequence of chemical reactions which are believed to be responsible for
15 molecular averaging of the paraffins.

16
17 As an example, the following is the general sequence of reactions for ethylene
18 and a C₂₀ paraffin, where the C₂₀ paraffin is first dehydrogenated to form an
19 olefin and combined with ethylene, the two olefins are molecularly averaged,
20 and, in this example, the resulting metathesized olefins are hydrogenated to
21 form paraffins:



Refractory Materials

31 In most cases, the metals in the catalyst mass (dehydrogenation and olefin
32 metathesis) will be supported on a refractory material. Refractory materials

1 suitable for use as a support for the metals include conventional refractory
2 materials used in the manufacture of catalysts for use in the refining industry.
3 Such materials include, but are not necessarily limited to, alumina, zirconia,
4 silica, boria, magnesia, titania and other refractory oxide material or mixtures
5 of two or more of any of the materials. The support may be a naturally
6 occurring material, such as clay, or synthetic materials, such as silica-alumina
7 and borosilicates. Molecular sieves, such as zeolites, also have been used as
8 supports for the metals used in carrying out the dual functions of the catalyst
9 mass. See, for example, U.S. Patent No. 3,668,268. Mesoporous materials
10 such as MCM-41 and MCM-48, such as described in Kresge, C.T., et al.,
11 *Nature* (Vol. 359) pp. 710-712, 1992, may also be used as a refractory
12 support. Other known refractory supports, such as carbon, may also serve as
13 a support for the active form of the metals in certain embodiments. The
14 support is preferably non-acidic, i.e., having few or no free acid sites on the
15 molecule. Free acid sites on the support may be neutralized by means of
16 alkali metal salts, such as those of lithium. Alumina, particularly alumina on
17 which the acid sites have been neutralized by an alkali salt, such as lithium
18 nitrate, is usually preferred as a support for the
19 dehydrogenation/hydrogenation component, and silica is usually preferred as
20 the support for the metathesis component. The preferred catalyst/support for
21 the dehydrogenation step is Pt/silicalite, as this combination is believed to
22 show the best resistance to fouling.

23
24 The amount of active metal present on the support may vary, but it must be at
25 least a catalytically active amount, i.e., a sufficient amount to catalyze the
26 desired reaction. In the case of the dehydrogenation/hydrogenation
27 component, the active metal content will usually fall within the range from
28 about 0.01 weight percent to about 50 weight percent on an elemental basis,
29 with the range of from about 0.1 weight percent to about 20 weight percent
30 being preferred. For the olefin metathesis component, the active metals
31 content will usually fall within the range of from about 0.01 weight percent to

1 about 50 weight percent on an elemental basis, with the range of from about
2 0.1 weight percent to about 25 weight percent being preferred.

3

4 Since only the C₂₀+ wax fraction is subjected to dehydrogenation conditions,
5 the dehydrogenation catalyst and the olefin metathesis catalyst are typically
6 present in separate reactors. However, for olefin metathesis catalysts which
7 can tolerate the presence of the hydrogen generated in the dehydrogenation
8 step, it may be possible to perform both steps in a single reactor. In a reactor
9 having a layered fixed catalyst bed, the two components may, in such an
10 embodiment, be separated in different layers within the bed.

11

12 If it is desirable to hydrogenate the olefins from the molecular averaging
13 chemistry, it may be necessary to include an additional hydrogenation step in
14 the process, since the hydrogenation of the olefins must take place after the
15 molecular averaging step.

16

17 Isomerization Chemistry

18

19 Optionally, the fractions being molecularly averaged or the products of the
20 molecular averaging chemistry are isomerized, so that the products have
21 more branched paraffins, thus improving their pour, cloud and freeze points.
22 Isomerization processes are generally carried out at a temperature between
23 200°F and 700°F, preferably 300°F to 550°F, with a liquid hourly space
24 velocity between 0.1 and 2, preferably between 0.25 and 0.50. The hydrogen
25 content is adjusted such that the hydrogen to hydrocarbon mole ratio is
26 between 1:1 and 5:1. Catalysts useful for isomerization are generally
27 bifunctional catalysts comprising a hydrogenation component (preferably
28 selected from the Group VIII metals of the Periodic Table of the Elements,
29 and more preferably selected from the group consisting of nickel, platinum,
30 palladium and mixtures thereof) and an acid component. Examples of an acid
31 component useful in the preferred isomerization catalyst include a crystalline

1 zeolite, a halogenated alumina component, or a silica-alumina component.
2 Such paraffin isomerization catalysts are well known in the art.

3

4 Optionally, but preferably, the resulting product is hydrogenated. The
5 hydrogen can come from a separate hydrogen plant, can be derived from
6 syngas, or made directly from methane and other light hydrocarbons.

7

8 After hydrogenation, which typically is a mild hydrofinishing step, the resulting
9 distillate fuel product is highly paraffinic. Hydrofinishing is done after
10 isomerization. Hydrofinishing is well known in the art and can be conducted
11 at temperatures between about 190°C to about 340°C, pressures between
12 about 400 psig to about 3000 psig, space velocities (LHSV) between about
13 0.1 to about 20, and hydrogen recycle rates between about 400 and
14 1500 SCF/bbl.

15

16 The hydrofinishing step is beneficial in preparing an acceptably stable
17 distillate fuels. Distillate fuels that do not receive the hydrofinishing step may
18 be unstable in air and light due to olefin polymerization. To counter this, they
19 may require higher than typical levels of stability additives and antioxidants.

20

21 The process will be readily understood by referring to the flow diagram in the
22 figure. In the flow scheme contained in the figure, the process of the present
23 invention is practiced in batch operation. However, it is possible to practice
24 the present invention in continuous operation.

25

26 Box 10 is a reactor that reacts syngas in the presence of an appropriate
27 Fischer-Tropsch catalyst to form Fischer-Tropsch products. These products
28 are fractionally distilled (Box 20), and a light gas/naphtha fraction is sent to a
29 reactor (Box 70) for molecular averaging. A C₅₋₂₀ fraction is isolated in
30 Box 30, and a relatively high molecular weight (C₂₀₊) fraction is sent to a
31 reactor for dehydrogenation (Box 40), then a reactor (Box 70) for molecular

-40-

1 averaging. Following molecular averaging, the reaction mixture is fractionally
2 distilled (Box 20) and the desired product isolated in Box 30. Following
3 product isolation, the product can optionally be isomerized (Box 50) and
4 blended (Box 60) to form a desired distillate fuel composition.

5

6 The following examples will help to further illustrate the invention but are not
7 intended to be a limitation on of the scope of the process.

8

9

Example 1

10

11 A petroleum derived C₃₀-C₂₀₀ linear hydrocarbon feedstock that includes at
12 least 70 wt.% linear paraffins with up to 50 mole% of oxygenates (e.g. linear
13 alcohols) wax is dehydrogenated as follows. The linear hydrocarbon feed is
14 fed to a hydrotreater containing a packed bed of platinum on alumina catalyst.
15 Hydrogen is fed to the hydrotreater at a ratio of about 3,000 SCF per Bbl of
16 linear hydrocarbon feed. The hydrotreater is operated at a temperature of
17 about 600°F to 650°F (316°C to 343°C), a pressure of about 10 atm to
18 120 atm, and a liquid space velocity (LHSV) of about 0.5 hr⁻¹ to 1 hr⁻¹. The
19 hydrotreater hydrogenates olefins and oxygenates (e.g., alcohols) in the feed
20 to the corresponding paraffins and converts organics sulfur and nitrogen
21 compounds to hydrogen sulfide and ammonia which are preferably removed
22 from the liquid reaction products as gases along with hydrogen and scrubbed
23 out of the hydrogen gas.

24

25 The entire hydrogenated product is fed to a vapor/liquid separator where the
26 gas phase (hydrogen, ammonia, hydrogen sulfide, and any light
27 hydrocarbons, e.g., C₁-C₂ alkanes) is separated and discharged. The
28 hydrogenated C₃₀-C₂₀₀ hydrocarbon liquid phase is fed to a dehydrogenation
29 reactor along with recycled hydrogen and, if needed, any made-up hydrogen.
30 Hydrogen is supplied to the reactor at a ratio of about 1,000 SCF of hydrogen
31 per barrel of hydrocarbon feed, including any recycle. The dehydrogenation

1 reactor is a fixed bed reactor containing 0.5 wt. % platinum on alumina
2 catalyst bed. The reactor is initially operated at a LHSV of about 40 hr⁻¹, a
3 temperature of about from 700°F to 750°F (371°C to 399°C), and a pressure
4 of about 2 atm. The conditions can be adjusted as needed to give about a
5 30% conversion of paraffin to internal olefins. For example, higher LHSVs
6 and lower temperatures give lower conversions and vice versa. The entire
7 reaction product is fed to a vapor/liquid separator where the hydrogen is taken
8 off. A portion of the hydrogen is recycled back to the dehydrogenation reactor
9 and the remainder can be used for other plant purposes.

10

11 The liquid reaction product is fed to a fixed bed olefin metathesis reactor
12 containing a catalyst bed that includes a metathesis catalyst, such as
13 tungsten on silica. Low molecular weight olefins, such as those from a
14 Fischer-Tropsch reaction, are also fed to the reactor at a suitable mole ratio of
15 low molecular weight olefins to wax olefins such that the average molecular
16 weight of the reactants is in a desired range. As in the case of the
17 dehydrogenation reaction, the reaction conditions may be adjusted as needed
18 to provide the desired conversion.

19

20 The reaction product is fed to a fractional distillation column and a desired
21 fraction is isolated. The product can be hydrotreated if desired, preferably
22 using syngas or recycled hydrogen as the hydrogen source. Unreacted low
23 molecular weight hydrocarbons and wax hydrocarbons can be recycled back
24 to the dehydrogenation reactor and/or to the olefin metathesis reactor.

25

26 Example 2

27

28 An integrated syngas, Fischer-Tropsch and molecular averaging process
29 starting from natural gas is described. Impurities in natural gas are removed
30 by passing the gas through an amine scrubber and a sulfur scrubber. The
31 amine scrubber removes acid gases such as hydrogen sulfide, mercaptans

1 and carbon dioxide. The sulfur scrubber contains a packed bed of zinc oxide
2 and removes any traces of sulfur gases, e.g., hydrogen sulfide or mercaptan
3 gases remaining in the natural gas.

4

5 The treated natural gas is fed, together with steam, to a syngas reactor where
6 it is reacted with air or oxygen to effect partial oxidation of the methane. The
7 fixed bed reactor contains a methane reforming, nickel-based catalyst and is
8 operated at a temperature between 400°C and 600°C, at a pressure of
9 between 15 and 30 bar, and at a space velocity of about 8,000 hr⁻¹. The
10 resulting syngas contains between 1.8 and 3.5 moles of hydrogen per mole of
11 carbon monoxide. If needed, the mole ratio of hydrogen to carbon monoxide
12 may be adjusted by using more steam, adding a carbon dioxide rich stream or
13 passing the syngas through a membrane separator.

14

15 The syngas is fed to a Fischer-Tropsch bubble column slurry reactor
16 containing a 12 wt. % cobalt on low density alumina catalyst with a particle
17 size of about 25 to 65 microns and a density of about 0.4 to 7 g/cc in a 8 cs.
18 (100°C) synfluid slurry liquid. Before mixing with the slurry liquid, the catalyst
19 is reduced by contact with a 5 vol.% hydrogen, 95 vol. % nitrogen gas at about
20 200-250°C for about 12 hours. After contact with the hydrogen, the
21 temperature is increased to about 350-400°C, and this temperature is
22 maintained for about 24 hours while the hydrogen content of the gas is slowly
23 increased until the reducing gas is essentially 100% hydrogen. The reactor is
24 operated at a temperature between about 210°C and 230°C, a pressure of
25 25-30 bar, and a synthesis gas linear velocity of about 6 to 10 cm/sec. The
26 resulting liquid hydrocarbon product contains a high proportion of C₂₆ to C₅₀
27 paraffins (the wax product) and a light product boiling below about 650°F
28 (282°C) containing middle distillate and tail gases. Tail gases are removed
29 from the light fraction, for example, by using one or more liquid/gas separators
30 operating at lower temperatures and/or pressures and the remaining light
31 product stream (condensate) comprising C₅ and higher hydrocarbons boiling

1 below 650°F (343°C), which are predominantly olefins, are isolated and sent
2 to the olefin metathesis reactor.

3

4 The Fischer-Tropsch wax product is fractionated into a wax fraction boiling
5 above about 650°F (343°C), primarily containing C₂₆-C₅₀ linear paraffins, a
6 high boiling bright stock fraction boiling above about 1100°F, and a liquid fuel
7 fraction boiling below about 650°F. The C₂₆-C₅₀ linear paraffin fraction is fed
8 to a hydrotreater. Hydrogen is furnished to the hydrotreater at a ratio of about
9 500 SCF per Bbl of hydrocarbon feed. The hydrotreater is a fixed bed reactor
10 containing a 0.5 wt. % palladium on alumina catalyst. The hydrotreater is
11 operated at a LHSV of about from 0.5 to 1 hr⁻¹, a temperature in the range of
12 about 500°F to 550°F (260°C to 288°C), and a pressure of about
13 100-120 atms. The hydrotreater hydrogenates the oxygenates, e.g., linear
14 alcohols, and olefins in the feed to paraffins and converts any traces of
15 organic sulfur into hydrogen sulfide. The hydrogenated reaction product is fed
16 to liquid/vapor separator where the excess hydrogen and any hydrogen
17 sulfide is removed as the gaseous phase. Depending on the purity of the
18 hydrogen phase, it may be recycled back to the hydrotreater with makeup
19 hydrogen or may be first passed through one or more scrubbers, not shown,
20 before being recycled or used for other plant uses. The hydrogenated liquid
21 phase is discharged and fed to the dehydrogenation reactor along with any
22 recycle. Hydrogen is furnished to reactor at a ratio of about 1,000 SCF of
23 hydrogen per 1 Bbl of hydrocarbon feed including any recycle.

24

25 The dehydrogenation reactor includes a catalyst bed containing a 0.5 wt. %
26 platinum on silicalite catalyst. The dehydrogenation reactor is initially
27 operated at a reaction temperature of about 700°F to 790°F and a pressure of
28 about 2 atm and at a LHSV of about 35 hr⁻¹. The conditions then adjusted as
29 needed give a conversion of C₂₀-C₅₀ linear paraffin to internal olefin of about
30 30%. The dehydrogenation reaction product can be passed to a vapor/liquid
31 phase separator where hydrogen and any light gases, e.g., water vapor

1 generated by any trace oxygenates not hydrogenated in the hydrotreater, are
2 discharged. The liquid product includes both internal olefins and unreacted
3 paraffins and is sent to a molecular averaging reactor containing a 5 wt. %
4 tungsten on silica catalyst. It is combined with low molecular weight olefins
5 from the Fischer-Tropsch reaction.

6

7 The reaction mixture is then passed to a distillation column. Low molecular
8 weight olefins and unreacted C₃₀-C₅₀ hydrocarbons are taken off and recycled
9 back to either dehydrogenation reactor or, depending on the olefin content, to
10 the molecular averaging reactor. Product in the desired range is also isolated.

11

12 While the present invention has been described with reference to specific
13 embodiments, this application is intended to cover those various changes and
14 substitutions that may be made by those skilled in the art without departing
15 from the spirit and scope of the appended claims.

1 WHAT IS CLAIMED IS:

2

3 1. A process for preparing a distillate fuel composition, the process
4 comprising:

5

6 (a) combining a fraction with an average molecular weight below about
7 C₆ and which includes at least 20% olefins with a fraction with
8 average molecular weight above about C₂₀ which includes at least
9 10% olefins in a suitable proportion such that, when the molecular
10 weights of the fractions are averaged, the average molecular
11 weight is the desired molecular weight for a distillate fuel
12 composition;

13

14 (b) subjecting the olefins in the fractions to olefin metathesis to provide
15 a product with a desired molecular weight; and
16

17 (c) isolating the product.

18

19 2. The process of claim 1, wherein the fraction with an average molecular
20 weight below about C₆ is greater than 35 percent olefins.

21

22 3. The process of claim 1, wherein the fraction with an average molecular
23 weight below about C₆ is greater than 50 percent olefins.

24

25 4. The process of claim 1, wherein the fraction with an average molecular
26 weight above about C₂₀ is between about 25 and 50 percent olefins.

27

28 5. The process of claim 1, wherein the fraction with an average molecular
29 weight above about C₂₀ is greater than 35 percent olefins.

30

- 1 6. The process of claim 1, wherein at least a portion of the fraction with
2 average molecular weight above about C₂₀ is obtained via a
3 Fischer-Tropsch process.
- 4 7. The process of claim 6, wherein at least a portion of the fraction with
5 average molecular weight above about C₂₀ is dehydrogenated prior to
6 the olefin metathesis step.
- 7
- 8 8. The process of claim 1, wherein at least a portion of one or both of the
9 fractions are derived from crude oil.
- 10
- 11 9. The process of claim 1, wherein the product is isolated via fractional
12 distillation.
- 13
- 14 10. The process of claim 1, wherein at least a portion of the product is
15 combined with an additive selected from the group consisting of
16 lubricants, emulsifiers, wetting agents, densifiers, fluid-loss additives,
17 corrosion inhibitors, oxidation inhibitors, friction modifiers, demulsifiers,
18 anti-wear agents, dispersants, anti-foaming agents, pour point
19 depressants, detergents, and rust inhibitors.
- 20
- 21 11. The process of claim 1, wherein one or more of the fractions are
22 obtained via a process other than Fischer-Tropsch chemistry, and the
23 fractions include heteroatoms, further comprising hydrotreating the
24 fraction(s) including heteroatoms to remove the heteroatoms prior to the
25 olefin metathesis reaction.
- 26
- 27 12. The process of claim 1, further comprising isomerizing at least a portion
28 of the product.
- 29
- 30 13. The process of claim 1, further comprising hydrogenating at least a
31 portion of the olefins in the product.

1 14. The process of claim 1, wherein the product has an average molecular
2 weight between C₅ and C₂₀.

3

4 15. The process of claim 1, wherein the product has a boiling point in the
5 range of between 68°F and 450°F.

6

7 16. The process of claim 1, wherein the product has a boiling point in the
8 range of between about 250°F and 370°F.

9

10 17. A process for preparing a distillate fuel composition, the process
11 comprising:

12

13 (a) performing Fischer-Tropsch synthesis on syngas to provide a
14 product stream;

15

16 (b) fractionally distilling the product stream and isolating a C₂₋₆ fraction
17 and a C₂₀₊ fraction;

18

19 (c) dehydrogenating or partially dehydrogenating the C₂₀₊ fraction;

20

21 (d) combining the dehydrogenated or partially dehydrogenated C₂₀₊
22 fraction with the C₂₋₆ fraction in a suitable proportion such that,
23 when the molecular weights of the fractions are averaged, the
24 average molecular weight is between approximately C₅ and C₂₀;

25

26 (e) subjecting the olefins in the fractions in step (e) to olefin
27 metathesis; and

28

29 (f) isolating a product in the C₅₋₂₀ range.

30

- 1 18. The process of claim 17, further comprising isomerizing at least a portion
2 of the product.
- 3
- 4 19. The process of claim 17, further comprising hydrotreating at least a
5 portion of the olefins in the product.
- 6
- 7 20. The process of claim 17, further comprising blending at least a portion of
8 the product with one or more additional distillate fuel compositions.
- 9
- 10 21. The process of claim 17, further comprising blending at least a portion of
11 the product with one or more additives selected from the group
12 consisting of lubricants, emulsifiers, wetting agents, densifiers, fluid-loss
13 additives, corrosion inhibitors, oxidation inhibitors, friction modifiers,
14 demulsifiers, anti-wear agents, dispersants, anti-foaming agents, pour
15 point depressants, detergents, and rust inhibitors.
- 16
- 17 22. A process for preparing a distillate fuel composition, the process
18 comprising:
19
- 20 (a) performing Fischer-Tropsch synthesis on syngas using a catalyst
21 which provides low to moderate chain growth probabilities to
22 provide a product stream including at least 5% C₂₋₈ olefins;
- 23
- 24 (b) performing Fischer-Tropsch synthesis on syngas using a catalyst
25 which provides high chain growth probabilities to provide a product
26 stream including predominantly C₂₀₊ paraffins;
- 27
- 28 (c) dehydrogenating or partially dehydrogenating the C₂₀₊ paraffinic
29 product stream;
- 30 (d) combining the dehydrogenated or partially dehydrogenated C₂₀₊
31 product stream with the C₂₋₈ product stream in a suitable proportion

1 such that, when the molecular weights of the fractions are
2 averaged, the average molecular weight is between approximately
3 C₅ and C₂₀;

4

5 (e) subjecting the olefins in the fractions in step (d) to olefin
6 metathesis; and

7

8 (f) isolating a product in the C₅₋₂₀ range.

9

10 23. The process of claim 22, wherein the C₂₋₈ product stream from the
11 Fischer-Tropsch synthesis step includes at least 10% olefins.

12

13 24. The process of claim 22, wherein the C₂₋₈ product stream from the
14 Fischer-Tropsch synthesis step includes at least 20% olefins.